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| (51) International Patent Classification 5 :<br><br>C08F 214/26, H01B 3/44   | A1   | (11) International Publication Number: WO 90/15828<br><br>(43) International Publication Date: 27 December 1990 (27.12.90) |
| (21) International Application Number: PCT/US90/03485<br><br>(22) International Filing Date: 20 June 1990 (20.06.90)<br><br>(30) Priority data:<br>368,638 20 June 1989 (20.06.89) US<br><br>(71) Applicant: RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Menlo Park, CA 94025 (US).<br><br>(72) Inventors: DAHL, Klaus, J.; 136 Austin Avenue, Atherton, CA 94027 (US). JANSONS, Viktors; 123 New York Avenue, Los Gatos, CA 95030 (US).<br><br>(74) Agents: BURKARD, Herbert, G. et al.; Raychem Corporation, 300 Constitution Drive, Menlo Park, CA 94025 (US). | (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).<br><br>Published<br><i>With international search report.<br/>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |  |

(54) Title: THERMOPLASTIC FLUOROPOLYMERS

(57) Abstract

A thermoplastic fluoropolymer which has improved tensile strength, yield strength, and cut-through resistance at elevated temperature. In a preferred embodiment, the fluoropolymer is an ionomer which comprises at least 40 mole percent perfluorinated repeat units and at least 0.4 mole percent repeat units which contain at least one anion of a salt group. Fluoropolymers of the invention are particularly useful for airframe wire.

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THERMOPLASTIC FLUOROPOLYMERSBACKGROUND OF THE INVENTION5    Cross-Reference to Related Applications

This application is a continuation-in-part of Application Serial No. 07/368,638, filed June 20, 1989, the disclosure of which is incorporated herein by reference.

10    Field of the Invention

This invention relates to thermoplastic fluoropolymers.

Introduction to the Invention

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Thermoplastic fluoropolymers such as ethylene-tetrafluoroethylene polymers (ETFE) have a combination of physical, chemical, and electrical properties which makes them useful for many applications. Such polymers are particularly useful for electrically insulating and environmentally protecting electrical conductors, particularly electrical conductors such as air frame wires, computer cables, and automotive cables. Reference may be made, for example, to U.S. Patent Nos. 4,155,823, 4,353,961, 4,521,485, 4,678,709, and 4,624,990, and copending commonly assigned application Serial No. 07/338,914 (Lunk et al), filed April 17, 1989, the disclosures of which are incorporated herein by reference.

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Although these fluoropolymers are generally useful at room temperature, they suffer from the problem that their physical properties deteriorate sharply at elevated temperatures, even at temperatures well below their melting points. The tensile strength and modulus of the polymers at elevated temperature can be improved by the addition of reinforcing fillers, but such reinforced polymers have low elongation properties, exhibit increased specific gravity, and have high melt viscosities. This combination is detrimental, especially when the polymer is to be used to coat air frame wire. Such wiring must be light-weight, is generally applied in a thin coating over the wire, and must be resistant to puncturing by a broken strand of wire (i.e. have good cut-through resistance). Thus it is desirable to have a polymer which can be formed over the wire in a thin, pinhole-free layer which conforms to, but is not penetrated by, a strand of the wire.

SUMMARY OF THE INVENTION

We have now discovered that thermoplastic fluoropolymers with improved mechanical  
5 properties and good melt-flow properties can be made. In a first aspect, this invention provides an  
ionomer which comprises a thermoplastic fluoropolymer which

- (A) has a yield strength at 150°C of at least 400 psi (2.76 MPa);  
10 (B) has a tensile strength at 150°C of at least 3500 psi (24.1 MPa); and  
(C) fulfills at least one of the following conditions
    - (1) it is electrically insulating;
    - 15 (2) when saturated with water it contains less than 5 percent by weight of water;  
and
    - (3) it does not track when tested in accordance with ASTM D3638.
- 20 In a second aspect, this invention provides a thermoplastic fluoropolymer which
- (A) is an ionomer which comprises
    - 25 (1) at least 40 mole percent perfluorinated repeat units; and
    - (2) at least 0.4 mole percent repeat units which contain at least one anion of a salt group;
  - (B) has a yield strength at 150°C of at least 400 psi (2.76 MPa); and  
30 (C) has a tensile strength at 150°C of at least 2000 psi (13.8 MPa); and  
(D) fulfills at least one of the following conditions
    - 35 (1) it is electrically insulating;

- (2) when saturated with water it contains less than 5 percent by weight of water; and
- (3) it does not track when tested in accordance with ASTM D3638.

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In a third aspect, this invention provides an insulated wire which is at least partly coated by a polymer of the first or second aspects of the invention. In a fourth aspect, this invention provides a method of making the polymers of the first and second aspects of the invention.

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#### DETAILED DESCRIPTION OF THE INVENTION

Thermoplastic fluoropolymers of the invention are those which contain by weight more than about 10% fluorine. Such polymers include homopolymers, copolymers such as ethylene-tetrafluoroethylene copolymers (ETFE), tetrafluoroethylene-hexafluoropropylene copolymers, 15 ethylene-chlorotrifluoroethylene copolymers, and mixtures of any of the above. The term "copolymer" includes terpolymers, e.g. a copolymer of ethylene, tetrafluoroethylene, and optionally a third monomer. Typically such copolymers contain about 30 to about 60 mole percent of ethylene, about 35 mole percent of tetrafluoroethylene, and about 0 to about 35 mole percent of one or more other comonomers. Preferably the third monomer is hexafluoropropylene; 3,3,3-trifluoropropylene-20 1; 2-trifluoromethyl-3,3,3-trifluoropropylene-1; or perfluoro(alkyl vinyl ether). Particularly preferred is ETFE. Commercially available ETFE copolymers are sold under the tradename "Tefzel" by E.I. duPont de Nemours and Company, and under the tradename "Neoflon" from Daikin Industries. For the fluoropolymers of the invention, the molar ratio of -CF<sub>2</sub>-CF<sub>2</sub>- to -CH<sub>2</sub>-CH<sub>2</sub>- units when both are present is preferably from 40:60 to 60:40. Preferably the -CF<sub>2</sub>-CF<sub>2</sub>- and -CH<sub>2</sub>-CH<sub>2</sub>- units are in 25 substantially alternating sequence, i.e. at least 60%, preferably at least 75%, particularly at least 85%, especially at least 90%, e.g. 95% of the pairs of -CF<sub>2</sub>-CF<sub>2</sub>- and -CH<sub>2</sub>-CH<sub>2</sub>- units in the polymer are in alternating sequence. Although any number of different type of repeat units may be present, it is preferred that the fluoropolymer comprises at least 40 mole percent of perfluorinated repeat units, i.e. repeat units which each contain a group selected from -CF<sub>2</sub>-CF<sub>2</sub>-, -CF<sub>2</sub>-CF(CF<sub>3</sub>)-, -CH<sub>2</sub>-C(CF<sub>3</sub>)<sub>2</sub>-30 and -CF<sub>2</sub>-CF{O(CF<sub>2</sub>)<sub>n</sub>-(Z)}-, where Z is F or H and n is 1 to 4.

The polymers of the invention may be prepared by polymerization or copolymerization of an appropriate monomer or monomers in aqueous, nonaqueous, or mixed medium by the use of a free-radical initiator. Such polymerization of monomers is well known; see, for example, U.S. Patent Nos. 35 3,624,250; 4,123,602, and 4,166,165, the disclosures of which are incorporated herein by reference. The polymer may be isolated as a dispersion or powder which may be converted into extruded shapes, e.g. films, sheets, cubes, fibers, or filaments. For some embodiments, a preferred

method of making the polymer is by modifying a preformed precursor polymer, e.g. by refluxing or imbibing a material into the precursor such as polymer extruded onto a wire, or direct chemical modification. Alternatively, the compositions can be made by graft polymerization of the appropriate monomer or monomers onto a thermoplastic fluoropolymer in the form of a powder or a shaped precursor. When a melt-extrudable polymer precursor containing ester linkages or other acid group derivatives is obtained, it is possible to readily convert the precursor in the form of a powder or shaped article, e.g. coated conductor, to a metal salt in order to prepare an ionomer as hereinafter described.

The polymers of the invention are electrically insulating both when dry and when saturated with water. The volume resistivity of the dry polymer is preferably at least  $10^{10}$  ohm-cm, particularly at least  $10^{12}$  ohm-cm, especially at least  $10^{13}$  ohm-cm. If used as a wire insulation, the polymer on the wire preferably has a resistance, measured on a sample 1000 feet (305 meters) long, of at least 100 Mohm/1000 feet, particularly at least 500 Mohm/1000 feet, especially at least 1000 Mohm/1000 feet. The electrical insulation ability of the polymers on a wire are tested following the procedure of ASTM D3638. Preferably, the polymers, when tested under these conditions, do not track.

Polymers of the invention which are particularly preferred are those which are ionomers, i.e. thermoplastic polymers which contain both covalent and ionic bonds. The ionic bond results from the presence of a salt group, which may be contained in repeat units forming the main chain or in repeat units which are part of side chains which are pendant from the main chain. It is preferred that each of the salt groups is a salt of a carboxylic, sulfonic, or phosphonic acid. The salt groups may be different, but preferably are the same. Preferably the salt group has the formula  $-\langle X^p \rangle^q (M^r)^s$ , wherein X is the anion of an acid group, M is a cation, p and s each are 1 or 2, and q and r each are 1 to 6. The values of p and s may be the same or different and the values of q and r may be the same or different. In all cases,  $pq = rs$ .

The anion of the acid group X (also referred to as the acid anion or the anion of a salt group) is linked to the polymer chain through a direct bond or a divalent group in which there is a chain which consists of at least one carbon atom, at least one carbon atom and at least one oxygen atom, or at least one silicon and at least one carbon atom. In some embodiments, the divalent group linking the fluoropolymer chain to the acid anion of the salt group has the structure -R<sub>1</sub>-D<sub>1</sub>-R<sub>2</sub>- or -D<sub>1</sub>-R<sub>1</sub>-D<sub>2</sub>-R<sub>2</sub>- wherein each of R<sub>1</sub> and R<sub>2</sub> is a divalent substituted or unsubstituted aliphatic, alkylarylene or aromatic moiety or an organosilane moiety and each of D<sub>1</sub> and D<sub>2</sub> is a valence bond or -O-. R<sub>1</sub> and R<sub>2</sub>, as well as D<sub>1</sub> and D<sub>2</sub>, may be the same or different. Preferably at least 0.4 mole percent of the repeat units, particularly at least 0.8 mole percent, especially at least 1.0 mole percent, e.g. 2.0 to 4.0 mole percent, contain at least one anion of a salt group. It is preferred that the polymer comprises less than 10 mole percent, particularly less than 8.0 mole percent, especially less than 6.0 mole percent, e.g. 2.0 to 4.0 mole percent, of repeat units containing at least one anion of a salt group.

The cation M is selected from those cations which impart beneficial properties to the acid-containing fluoropolymer and which possess satisfactory stability at least in the service temperature range in which the fluoropolymer is normally used. The cation is normally metallic and normally 5 monovalent or divalent; in certain circumstances, tri-, tetra-, penta- or hexa-valent cations may be used. In particular, the mono- and divalent ions of the metals in groups IA, IB, IIA, IIB, IVA, and VIII are preferred. Suitable specific ions include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Y}^{3+}$ . Preferred monovalent or divalent cations are derived from sodium, potassium, lithium, calcium, barium, and zinc. It is generally preferred 10 that from 30 to 100% of acid groups be neutralized with metal ion, particularly from 40 to 60% of acid groups. However, if the fluoropolymer contains significant amounts of hydrogen-containing repeat units, especially on the chain connecting the acid group to the polymer backbone, it is preferred that any phosphonic and sulfonic acid groups be substantially neutralized, e.g. 100% neutralized.

15 Ionomers of the invention generally comprise both a salt and some free acid. Thus it is preferred that when the polymer comprises x mole percent of repeat units which contain at least one anion of a salt group and y mole percent repeat units which contain at least one acid group, x is at least 0.4, preferably at least 1.5, y is at most 8, preferably at most 7, particularly at most 6, especially at most 5, and (x + y) is at most 8.4, preferably at most 7.4, particularly at most 6.4.

20 As previously stated, the ionizable acid groups may be introduced by copolymerization of the unsaturated acid or suitable derivative, provided the monomer is substantially free of the telogenic activity during polymerization to form the polymer or by grafting onto the already-formed polymer. Unsaturated termonomers for both these methods suitable for use in the preparation of alternating 25 ethylene-tetrafluoroethylene copolymer include, but are not limited to, compounds of the general formula A - B - G, where A is a copolymerizable group, B is a connecting group or linkage, and G is an acid precursor group.

The A groups may comprise one or more of the following:  $\text{CH}_2=\text{CH}-$ ;  $\text{CF}_2=\text{CF}-$ ;  $\text{CF}_2=\text{CH}-$ ; 30  $\text{O}=\text{C}[\text{CF}_3,(\text{CF}_2)_t]-$ , where t is 1 or 2; and the like.

The B groups act as connectors linking the polymerizable A groups to the functionalized G groups. Such connecting groups comprise divalent substituted or unsubstituted aliphatic, alkylarylene or aromatic moieties which may include ether linkages or an organosilane moiety and are 35 selected to have:

1. low telogenic activity, i.e. little or no chain transfer effect on the polymerization activity of the A group, and limited, if any, interference with the desired 1:1 alternation in the synthesis of alternating copolymers;
- 5 2. thermal and oxidative stability which is at least approximately equal to that of the most sensitive repeat units in the polymer chain;
- 10 3. limited or no adverse effect on at least those properties of the polymer useful in service applications, especially when compared with the properties of a comparable copolymer not containing salt groups;
4. enhanced compatibility with the comonomers, oligomers and the final copolymer.

In addition it is advantageous to provide monomers which may be obtained using routes which are attractive both synthetically and commercially.

Such connecting groups (B) include but are not limited to: a carbon-carbon bond, an ether linkage and divalent perfluoroalkylene groups of up to 4 carbon atoms, optionally linked to an aliphatic chain of up to 6 carbon atoms or m- or p-phenylene, or linked through an ether oxygen to a perfluoroalkylene chain of up to 4 carbon atoms, divalent oxy-perfluoroalkylene groups of up to 6 carbon atoms, optionally linked to an aliphatic chain of up to 6 carbon atoms or m- or p-phenylene, or linked through a second oxygen atom to a perfluoroalkylene chain of up to 4 carbon atoms. Illustrative of these groups are -(CF<sub>2</sub>)<sub>(1 to 4)</sub>-E- where E is -(CH<sub>2</sub>)<sub>(2 to 6)</sub>- or m- or p-phenylene; -O-(CF<sub>2</sub>)<sub>(1 to 4)</sub>-E-; -CF<sub>2</sub>-CF(CF<sub>3</sub>)-E-; -O-C(CF<sub>3</sub>)<sub>2</sub>-(CF<sub>2</sub>)<sub>(1 to 4)</sub>-E-; -OCF<sub>2</sub>-CF(CF<sub>3</sub>)-E-; -O-CF(CF<sub>3</sub>)-CF<sub>2</sub>-E-; -(CF<sub>2</sub>)<sub>(1 to 4)</sub>-O-E' where E' is -(CH<sub>2</sub>)<sub>(3 to 6)</sub>- or m- or p-phenylene; -O-(CF<sub>2</sub>)<sub>(2 to 6)</sub>-E'; -CF<sub>2</sub>-CF(CF<sub>3</sub>)-O-E'; -O-E'; -(CF<sub>2</sub>)<sub>(1 to 4)</sub>-C(CF<sub>3</sub>)<sub>2</sub>-O-E'; -(CF<sub>2</sub>)<sub>(1 to 4)</sub>-C(CF<sub>3</sub>)<sub>2</sub>-O-E'; -O-C(CF<sub>3</sub>)<sub>2</sub>-(CF<sub>2</sub>)<sub>(1 to 4)</sub>-O-E'; -O-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-E'; -O-CF<sub>2</sub>-CF(CF<sub>3</sub>)-O-E'; -(CF<sub>2</sub>)<sub>(1 to 4)</sub>-C(CF<sub>3</sub>)<sub>2</sub>-E'' where E'' is -(CH<sub>2</sub>)<sub>(1 to 6)</sub>- or m- or p-phenylene; -O-C(CF<sub>3</sub>)<sub>2</sub>-E''; -(CF<sub>2</sub>)<sub>(1 to 4)</sub>-O-C(CF<sub>3</sub>)<sub>2</sub>-E''; -O-(CF<sub>2</sub>)<sub>(1 to 6)</sub>-O-C(CF<sub>3</sub>)<sub>2</sub>-E''; -(CF<sub>2</sub>)<sub>(1 to 4)</sub>-C(CF<sub>3</sub>)<sub>2</sub>-E''; and the like.

G groups include but are not limited to: -C(=O)-OR where R is -H, -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -CH(CF<sub>3</sub>)<sub>2</sub>, -CH<sub>2</sub>(CF<sub>2</sub>)<sub>(1 to 10)</sub>-F, -CH<sub>2</sub>(CF<sub>2</sub>)<sub>(1 to 10)</sub>-H, -Ph (i.e. phenyl), -perfluorophenyl, -Si(CH<sub>3</sub>)<sub>3</sub>; or -C(C=O)R' where R' is alkyl or fluoroalkyl; -C(OR)<sub>3</sub>; -C(=O)F; -SO<sub>2</sub>F; -SO<sub>3</sub>R; -P(=O)(OR)<sub>2</sub>; -P(=O)(R')-OR; -P(=O)(NR<sub>2</sub>)<sub>2</sub>; -P(=O)(NHR)<sub>2</sub>; -P(=O)(NH<sub>2</sub>)<sub>2</sub>; -P(=O)(R)NH<sub>2</sub>; -C(=O)NR<sub>2</sub>; -C(=O)NHR; -C(=O)NH<sub>2</sub>; -SO<sub>2</sub>NR<sub>2</sub>; -SO<sub>2</sub>NHR; -SO<sub>2</sub>NH<sub>2</sub>; -cyano; and the like.

Preferred termonomers include  $\text{CF}_2=\text{CF}-\text{O}-\text{Ph}'-\text{C}(=\text{O})-\text{OR}''$  where  $\text{Ph}'$  is m- or p-phenylene and where  $\text{R}''$  is - $\text{CH}_3$  or - $\text{CH}_2\text{CH}_3$ , - $\text{CH}(\text{CF}_3)_2$ , - $\text{Si}(\text{CH}_3)_3$ , - $\text{CH}_2(\text{CF}_2)(1 \text{ to } 10)-\text{F}$ , - $\text{CH}_2(\text{CF}_2)(1 \text{ to } 10)-\text{H}$ , - $\text{Ph}$ , pentafluorophenyl or - $\text{C}(=\text{O})\text{R}'$  where  $\text{R}'$  is alkyl or fluoroalkyl;  $\text{CF}_2=\text{CF}-\text{CF}_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-(\text{CF}_2)(1 \text{ to } 4)-\text{C}(\text{CH}_3)_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{OCF}_2-\text{C}(\text{CF}_3)_2-\text{O}-\text{Ph}'-\text{C}(=\text{O})\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{OCF}(\text{CF}_3)-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{OCF}_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{O}(\text{CF}_2)(1 \text{ to } 4)\text{C}(\text{CH}_3)_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-(\text{CF}_2)_2-\text{C}(\text{CF}_3)_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{CF}_2-\text{O}-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{CF}_2\text{CF}_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{CF}_2-(\text{CH}_2)(2 \text{ to } 6)-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{CF}_2-\text{O}-(\text{CH}_2)(3 \text{ to } 6)-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{CF}_2\text{CF}_2-\text{O}-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{OCF}(\text{CF}_3)\text{CF}_2-\text{O}-\text{Ph}'-\text{C}(=\text{O})\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{CF}_2-\text{O}-\text{C}(\text{CF}_3)_2-\text{Ph}'-\text{C}(=\text{O})-\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{OCF}_2\text{C}(\text{CF}_3)_2-\text{Ph}'-\text{C}(=\text{O})\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{CF}_2\text{C}(\text{CF}_3)_2-\text{O}-\text{Ph}'-\text{C}(=\text{O})\text{OR}$ ;  $\text{CF}_2=\text{CF}-\text{OCF}_2-(\text{CH}_2)(2 \text{ to } 6)-\text{C}(=\text{O})-\text{OR}$ ; and the like.

In all of the above monomers the  $\text{CF}_2=\text{CF}-$  group can be replaced by  $\text{CH}_2=\text{CH}-$  or  $\text{CH}_2=\text{CH}-\text{CH}_2$ . The allylic group requires attachment to electron withdrawing groups such as - $\text{CF}_2-$ , - $\text{OCF}_2-$ , - $\text{OCF}(\text{CF}_3)-$  or - $\text{OC}(\text{CF}_3)_2-$ .

The - $\text{C}(=\text{O})-\text{OR}$  group in the above monomers may be replaced by - $\text{C}(\text{OR})_3$ ;  $\text{P}(\text{=O})(\text{OR})_2$ ; - $\text{SO}_2\text{F}$ ; or - $\text{SO}_3\text{R}$ . Other sulfonic acid derivatives include but are not limited to  $\text{CF}_2=\text{CF}-\text{SO}_2\text{F}$ ;  $\text{CF}_2=\text{CF}-\text{SO}_3\text{R}$ ;  $\text{CF}_2=\text{CF}-(\text{CF}_2)(1 \text{ to } 6)-\text{SO}_2\text{F}$ ;  $\text{CF}_2=\text{CF}-(\text{CF}_2)(1 \text{ to } 6)-\text{SO}_3\text{R}$ ;  $\text{CH}_2=\text{CH}-(\text{CF}_2)(1 \text{ to } 6)-\text{SO}_2\text{F}$ ;  $\text{CH}_2=\text{CH}-(\text{CF}_2)(1 \text{ to } 6)-\text{SO}_3\text{R}$ ;  $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-(\text{CF}_2)(1 \text{ to } 6)-\text{SO}_2\text{F}$ ;  $\text{CF}_2=\text{CF}-\text{O}-\text{CF}(\text{CF}_3)\text{CF}_2-\text{O}-(\text{CF}_2)(1 \text{ to } 6)-\text{SO}_3\text{R}$ ;  $\text{CF}_2=\text{CF}-\text{O}-\text{C}(\text{CF}_3)_2-\text{CF}_2-\text{SO}_3\text{R}$ ; and the like. Preferred monomers include  $\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)(1 \text{ to } 6)-\text{SO}_2\text{F}$ .

In instances where the salts of these copolymers do not have sufficient thermal stability for melt processing, their precursors (e.g. esters, ortho esters, amides or nitriles) may be melt-formed and the precursor groups in the shaped polymers converted to salt groups. Thus, for example, a polymer comprising the precursor can be extruded or otherwise coated onto a wire, and the precursor converted in situ into the salt.

If a perfluorinated chain polymer of the invention, for example one derived from tetrafluoroethylene, is desired, the monomer is selected from those compounds having a copolymerizable moiety comprising one of  $\text{CF}_2=\text{CF}-\text{O}-$ ,  $\text{CF}_2=\text{CF}-\text{CF}_2-$ ,  $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2-$  and  $\text{CF}_2=\text{CF}-\text{O}-\text{Ph}'-$ .

This invention also contemplates the attachment of ionic groups or precursors of ionic groups to a thermoplastic fluoropolymer such as ETFE. This may be carried out in a number of ways, e.g.

functionalization of thermoplastic fluoropolymers, grafting of unsaturated compounds to thermoplastic fluoropolymers, or a combination of grafting and functionalization.

#### A. FUNCTIONALIZATION OF THERMOPLASTIC FLUOROPOLYMER

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This may be achieved by:

1. Nitrene or carbene insertion between C-H bonds by (a) reaction with sulfonylazides bearing functional groups (i.e. an ionomer precursor), or by (b) reaction with diazomalonates;
- 10 2. Chlorosulfonation which may be carried out by imbibing  $\text{SO}_2\text{Cl}_2$ ,  $\text{SO}_2\text{FCl}$ , or  $\text{SO}_2\text{F}_2$  followed by irradiation with or by oxidative sulfonation with  $\text{SO}_2/\text{air}$  and simultaneous irradiation with electrons.
- 15 3. Friedel-Crafts reaction of the thermoplastic fluoropolymer in the presence of  $\text{SbF}_5$  with unsaturated compounds, such as  $\text{CF}_2=\text{CFSO}_2\text{F}$  or  $\text{CF}_2=\text{CFCF}_2\text{SO}_2\text{F}$  to form pendant groups by addition of cationic sites on the polymer across the ethylenic double bonds of the monomer.
- 20 4. Direct attachment to pre-formed micelles of ionomeric surfactants bearing reactive groups, for example,  $(\text{CF}_2=\text{CF-O-CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CO}_2)_2\text{Zn}$  or  $\text{CF}_2=\text{CF-O-CF}_2-\text{CF}(\text{CF}_3)-\text{O-CF}_2\text{CF}_2\text{SO}_3^-\text{Na}^+$ , on irradiation.
- 25 5. Free radical substitution reactions with "non-polymerizable" monomers, such as fumarate esters, maleate esters, maleic anhydride,  $\text{CF}_2=\text{CF-C(CH}_3)_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CF}_3$ ,  $\text{CH}_2=\text{CH-C(CF}_3)_2\text{CH}_2\text{SO}_3\text{CH}_3$  and  $\text{CF}_3\text{CF=CFCF}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$ .

25

#### B. GRAFTING OF UNSATURATED COMPOUNDS TO THERMOPLASTIC FLUOROPOLYMERS

This may be carried out in a variety of ways, for example:

- 30 1. By exposure to radiation or by free radical initiation, for example, (a) pre-irradiation of thermoplastic fluoropolymer under  $\text{N}_2$  (preferably below the  $T_g$ ) followed by exposure to and reaction with monomers; (b) pre-irradiation of thermoplastic fluoropolymer containing a first monomer under  $\text{N}_2$  followed by exposure to and reaction with second monomers which contain ionic or ionic precursor groups; (c) pre-irradiation in air or  $\text{O}_2$  to form peroxide intermediates followed by heating or by sonification in the presence of monomers; (d) irradiation of polymer swollen with monomers preferably in the absence of oxygen; (f) use of special free radical initiators in the polymer melt such as high temperature activated and high boiling initiators including cumene hydroperoxide, t-butyl peroxy
- 35

- phthalic acid, ethyl-O-benzoyl laurohydroximate, perfluoroctyl iodide, bis(perfluoroalkyl)diazomethanes and perfluoroalkyl azides and high temperature resistant and high boiling monomers, or by melt reaction under pressure to minimize volatilization of low boiling compounds; or (g) direct attachment of thermoplastic fluoropolymer to pre-formed micelles of
- 5 ionomeric surfactants containing unsaturated groups or of ionomeric monomers in the presence of surfactants, by irradiation in the presence or in the absence of other polyfunctional monomers which may be used to enhance crosslinking of the polymer. Such polyfunctional monomers include triallyl isocyanurate or other compounds such as are disclosed in U.S. Patent Nos. 4,155,823 and 4,353,961 referenced hereinabove; and also in 4,121,001 (now reissued as 31103) and 4,176,027,
- 10 the disclosures of which are incorporated herein by reference. The reagents may also be dispersed in the polymer matrix as a microemulsion and then irradiated.

If required, the monomers may be dissolved in the polymer under pressure at elevated temperature. This is a method of choice for the incorporation of monomers into thermoplastic

15 fluoropolymer.

2. Ionic initiation which includes the use of (a) alkyl or aryl metal derivatives; and (b) ionizing radiation under anhydrous conditions.

20 C. GRAFTING AND FUNCTIONALIZATION

Both grafting and functionalization may be used, e.g. grafting with acenaphthylene, N-vinylcarbazole, I-(trifluorovinyl)biphenyl, or I-(trifluoroethoxy)biphenyl, followed by sulfonation to give the arylsulfonic acid salt ionomers on subsequent neutralization.

- 25 As already indicated many of the termonomers listed above are suitable both for the copolymerization process of forming ionomer precursor copolymers and for the grafting approach. However, the reactivity requirements for graft monomers are much less restrictive than for copolymerization termonomers. In grafting according to this invention, a single macro-radical addition step is preferred to produce isolated points of attachment of ionomer precursor groups. Chain growth to more than ten repeat units is undesirable; preferably growth is limited to less than five repeat units, for example two repeat units. Rapid chain transfer to the polymer trunk, followed by attachment of new graft units is most desirable for maximum graft yield with minimum graft chain length. Alternating graft copolymerization with a fluorinated monomer, such as hexafluoropropylene, and a more
- 30 electron-rich double bond monomer bearing the ionomer precursor payload yields thermooxidatively stable thermoplastic fluoropolymer-type graft chains with sufficiently spaced pendant payload groups
- 35

to optimize the improvement in physical properties by, for example, minimizing cyclic anhydride formation.

In addition, 1-monosubstituted or 1,1-disubstituted double bonds with groups of excessive steric hindrance toward chain propagation initiated by addition of a radical are also suitable for grafting, forming short graft chains, or for substitution on macroradicals.

Sufficient compatibility of grafting monomer with the thermoplastic fluoropolymer to enable bulk (as opposed to surface) grafting is essential. Solvents, inert to the reaction conditions, may be used to enhance grafting compatibility of otherwise poorly compatible monomers with the thermoplastic fluoropolymer. Long graft chains and secondary grafting on the already formed grafted chain to form branched pendant chains are undesirable. However, by first grafting with a suitable compatibilizing monomer which may contain acid or acid precursor groups and which forms linear chains on polymerization, the polymer can be rendered more compatible for subsequent grafting with a second monomer which contains salt, acid or acid precursor groups. The polymer, after the initial grafting step, often tends to retain residual radicals which may primarily be trapped in the crystalline regions of the polymer. If such a grafted polymer is immersed in a suitable second graftable monomer, which also may contain acid or acid precursor groups and which may comprise a polyunsaturated compound (i.e. a covalent crosslinking enhancer), and then heated, a substantial amount of post-irradiation grafting of the second monomer can occur. If necessary, of course, this second grafting step can be facilitated by further exposure of the polymer to ionizing radiation.

For irradiation of monomer-swollen polymer, stability of monomer and grafted products towards radiation is also important. Moreover, the monomer must not interfere with the normal radiation-induced activation of the polymer during the grafting process.

In addition to the above enumerated list of selected unsaturated graftable groups the following may be present in compounds for grafting to thermoplastic fluoropolymer:  $\text{CH}_2=\text{CH}-$ ,  $\text{CF}_2=\text{CF}-$ ,  $\text{CF}_2=\text{CH}-$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ,  $\text{CF}_2=\text{C}(\text{CF}_3)-$ , cyclohexenyl, cyclopentenyl, norbornenyl, 30 bicyclo[2.2.2]oct-2-enyl, 7-oxabicyclo[2.2.1]oct-2-enyl, maleimido, trans - $\text{C}=\text{C}$ - moieties and the like.

In addition to the connecting groups (B moieties) listed above, the following may advantageously be present in monomers for grafting to thermoplastic fluoropolymer: - $\text{E}''-$  [where  $\text{E}''$  is -(direct linkage),  $-(\text{CH}_2)(1 \text{ to } 6)-$ , or  $-\text{Ph}'-$ ];  $-\text{C}(\text{CH}_3)_2\text{E}''-$ ,  $-\text{C}(\text{CF}_3)_2\text{E}''-$  [where  $\text{E}''$  is  $-(\text{CH}_2)(1 \text{ to } 6)-$ , or  $-\text{Ph}'-$ ];  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{E}''-$  [where  $\text{E}''$  is  $-(\text{CH}_2)(2 \text{ to } 6)-$  or  $-\text{Ph}'-$ ];  $-\text{C}(\text{CF}_3)_2\text{O}\text{E}'$  [where  $\text{E}'$  is  $(\text{CH}_2)(3 \text{ to } 6)-$ , or  $-\text{Ph}'-$ ];  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}\text{E}'-$ ;  $-\text{Ph}'\text{Ph}'-$ ;  $-\text{Ph}'\text{O}\text{Ph}'-$ ;  $-\text{CH}_2\text{Si}(\text{CH}_3)_2\text{E}''-$ ,  $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{E}''-$ ,  $-1,1-$  cyclopentane-,  $-1\text{-methyl-1,3-cyclopentane}$ ,  $-1\text{-methyl-1,6-cyclohexane}$ ,  $-1,3\text{-cyclopentane}$ ,  $-1,1-$

cyclohexane-, -1,6-cyclohexane-, -1,6-dimethyl-1,6-cyclohexane-, -1,4-bicyclo[2.2.1]heptane-, -1,4-(7-oxabicyclo[2.2.1]heptane)-, -1,4-bicyclo[2.2.2]octane-, -C(=O)-Ph'-, -SO<sub>2</sub>-Ph'- and the like.

- Examples of preferred monomers for grafting thermoplastic fluoropolymers include, in addition to those listed above: CH<sub>2</sub>=C(CF<sub>3</sub>)-O-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-(CF<sub>2</sub>)<sub>n</sub>-Ph'-C(=O)-OR where n is 1 or 2, CF<sub>2</sub>=CF-O-(CF<sub>2</sub>)<sub>n</sub>-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-O-CF<sub>2</sub>CF(CF<sub>3</sub>)-O-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-O-C(CF<sub>3</sub>)<sub>2</sub>-Ph'-C(=O)-OR, CH<sub>2</sub>=CH-CH<sub>2</sub>-CF<sub>2</sub>CF<sub>2</sub>-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-(CF<sub>2</sub>)<sub>n</sub>-O-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-O-CF<sub>2</sub>CF<sub>2</sub>-O-Ph'-C(=O)-OR, CH<sub>2</sub>=CH-(CF<sub>2</sub>)<sub>n</sub>-O-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-O-Ph'-C(=O)-OR, CH<sub>2</sub>=CH-CH<sub>2</sub>-CF<sub>2</sub>-Ph'-C(=O)-OR, CH<sub>2</sub>=CH-(CF<sub>2</sub>)<sub>n</sub>-Ph'-C(=O)-OR, CF<sub>2</sub>=CFSO<sub>2</sub>F, CF<sub>2</sub>=CF-O-Ph'-SO<sub>2</sub>F, CF<sub>2</sub>=CF-O-PO<sub>3</sub>R<sub>2</sub>, CF<sub>2</sub>=C(CF<sub>3</sub>)-O-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-(CF<sub>2</sub>)<sub>n</sub>SO<sub>2</sub>F where n is 1 to 4, CF<sub>2</sub>=CF-O-(CF<sub>2</sub>)<sub>n</sub>SO<sub>2</sub>F where n is 1 to 4, CF<sub>2</sub>=CF-O-CF<sub>2</sub>CF(CF<sub>3</sub>)-O-CF<sub>2</sub>CF<sub>2</sub>-SO<sub>2</sub>F, and the like.

- In general, the above monomers are preferred because they (a) have adequate compatibility with thermoplastic fluoropolymers; (b) have a low tendency to undergo homopolymerization; (c) produce grafted polymers of sufficient thermo-oxidative stability; and (d) yield salt groups of sufficient thermal stability for melt processing.

- The following compounds are also suitable for use as grafting monomers: CH<sub>2</sub>=CH-C(CH<sub>3</sub>)<sub>2</sub>-C(=O)-OR, CH<sub>2</sub>=CH-C(CH<sub>3</sub>)<sub>2</sub>-(CH<sub>2</sub>)(1 to 4)-C(=O)-OR, CF<sub>2</sub>=CF-C(CH<sub>3</sub>)<sub>2</sub>-C(=O)-OR, CF<sub>2</sub>=CF-C(CH<sub>3</sub>)<sub>2</sub>-(CH<sub>2</sub>)(1 to 4)-C(=O)-OR, CH<sub>2</sub>=CH-C(CH<sub>3</sub>)<sub>2</sub>-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-C(CF<sub>3</sub>)<sub>2</sub>-O-Ph'-C(=O)-OR, CH<sub>2</sub>=CH-C(CF<sub>3</sub>)<sub>2</sub>-(CH<sub>2</sub>)(1 to 4)-C(=O)-OR and the like; fumarates and maleates, that is RO-C(=O)-CH=CH-C(=O)-OR, CH<sub>2</sub>=CH-C(=O)-OR, CH<sub>2</sub>=C(CH<sub>3</sub>)-C(=O)-OR, CF<sub>2</sub>=CF-Ph'-C(=O)-OR, CF<sub>2</sub>=CF-Ph'-SO<sub>2</sub>F, CF<sub>2</sub>=CF-Ph'-SO<sub>3</sub>R, CH<sub>2</sub>=CH-P(=O)(OR)<sub>2</sub>, N-maleimido-(CH<sub>2</sub>)(2 to 11)-C(=O)OR, CH<sub>2</sub>=CH-SO<sub>3</sub>R, CH<sub>2</sub>=CH-P(=O)(R'')-OR, CH<sub>2</sub>=CH-CH<sub>2</sub>-P(=O)(OR)<sub>2</sub>, CH<sub>2</sub>=CH-CH<sub>2</sub>-P(=O)(R'')-OR, CH<sub>2</sub>=CH-CH<sub>2</sub>-C(=O)-OR and amides, CH<sub>2</sub>=CH-CH<sub>2</sub>-C(=O)-O-C(=O)R''' (where -R''' is alkyl or fluoroalkyl), CH<sub>2</sub>=CH-CH<sub>2</sub>-C(OR)<sub>3</sub>, CH<sub>2</sub>=CH-CH<sub>2</sub>-SO<sub>2</sub>F, CH<sub>2</sub>=CH-CH<sub>2</sub>-SO<sub>3</sub>R, and amides and analogous nitriles corresponding to all the above esters and the like.

- The enhanced physical properties of the thermoplastic fluoropolymers of the invention are evident by determining the yield strength, the tensile strength, the percent elongation, the cut-through resistance, and the water uptake of these polymers. The physical properties of the polymers are directly dependent on chemical structure of the polymer backbone, the chemical structure of the connecting chain, and the identity of the acid anion and the metal cation. For example, the presence of electron-withdrawing groups (e.g. -CF<sub>2</sub>-) promotes decarboxylation, and thus a -CF<sub>2</sub>-C(=O)-O- structure is not preferred. Alternatively, the presence of free acid of a -SO<sub>3</sub>- group will produce a thermally unstable polymer. Thus the identity and amount of the substituents may be changed in order to control physical properties. Polymers of the invention have yield strengths at 150°C of at

least 400 psi (2.76 MPa), preferably at least 500 psi (3.45 MPa), particularly at least 550 psi (3.80 MPa), where yield strength is determined by ASTM Test D638.

- The tensile strength at 25°C of such polymers is at least 6000 psi (41.4 MPa), preferably at
- 5 least 7000 psi (48.3 MPa), particularly at least 8000 psi (55.2 MPa), e.g. 8500 to 9500 psi (58.7 to  
65.6 MPa). When measured at 150°C the tensile strength of such polymers is at least 3300 psi (22.8  
MPa), preferably at least 3500 psi (24.1 MPa), particularly at least 3700 psi (25.5 MPa), especially at  
least 4000 psi (27.6 MPa). When the polymer is in the form of an ionomer, the tensile strength at  
150°C is at least 2000 psi (13.8 MPa), preferably at least 2500 psi (17.3 MPa), particularly at least 3000  
psi (20.7 MPa), especially at least 3500 psi (24.1 MPa). At 150°C, the tensile strength of the polymer,  
whether or not in the form of an ionomer, is at most 8000 psi (55.2 MPa), preferably at most 7500 psi  
(51.6 MPa). The elongation of the polymers at 25°C is at least 80%, preferably at least 100%,  
particularly at least 120%, e.g. at least 140% to 150%. When measured at 150°C, the elongation of  
the polymer (whether or not in the form of an ionomer) is at least 150%, preferably at least 200%,  
15 particularly at least 250%, especially at least 300%, and at most 600%. The tensile strength and the  
percent elongation are determined by following the procedure of ASTM Test D638.

- If the polymer is covalently crosslinked, e.g. as a result of radiation or by chemical means, the  
yield strength at 150°C will be at least 400 psi (2.76 MPa), preferably at least 600 psi (4.14 MPa) and  
20 the tensile strength at 150°C will be at least 3300 psi (22.8 MPa), preferably at least 3500 psi (24.1  
MPa), particularly at least 4000 psi (27.6 MPa), and may be higher.

- The thermoplastic fluoropolymers of the invention have a cut-through resistance (CTR) which  
is substantially higher than conventional thermoplastic fluoropolymers. For example, conventional  
25 ethylene-tetrafluoroethylene copolymer (sold under the tradename Tefzel™ 2055 by DuPont) has a  
CTR at 150°C of approximately 0.4 lb/mil (71.6 kg/cm). Polymers of the invention have a CTR at 150°C  
of at least 0.5 lb/mil (89.5 kg/cm), preferably at least 0.6 lb/mil (107 kg/cm), particularly at least 0.7 lb/mil  
(125 kg/cm), especially at least 0.8 lb/mil (143 kg/cm), e.g. 0.9 to 1.3 lb/mil (161 to 232 kg/cm). The  
maximum cut-through resistance for polymers of the invention is generally at most 2.0 lb/mil (358  
kg/cm) when measured at 150°C. Cut-through resistance is measured on a sample of polymer which  
30 is in the form of a wire coated with approximately 0.008 inch (0.020 cm) of polymer and which is heated  
to a temperature of 150°C. The sample is laid between an anvil and a 90° included angle wedge-  
shaped weighted knife blade having a 0.005 inch (0.013 cm) flat section with a 0.005 inch (0.013 cm)  
radius edge. The anvil is hung by means of a stirrup from the load cell of an Instron™ tensile tester and  
35 the knife blade mounted on the movable bar of the tensile tester so that the blade edge lies  
transversely over the wire specimen. The knife edge is advanced towards the wire conductor at a rate  
of 0.2 inch/min (0.51 cm/min). Failure occurs when the knife edge contacts the conductor and the

resulting electrical contact causes the tensile tester to stop advancing the blade. The peak reading from the load cell is taken to be the cut-through resistance of the polymer on the wire.

In order to minimize weight increase and deterioration of electrical properties, it is desirable  
5 that the polymers of the invention have minimal water absorption. Water uptake is determined by weighing a sample of polymer before and after immersion in water at 90 to 100°C (i.e. boiling water) for 24 hours. The percent water uptake is defined as the percent change in weight from the start to the end of the test. Polymers of the invention have a water uptake of less than 5.0%, preferably less than 4.5%, particularly less than 4.0%, especially less than 3.0%, most especially less than 2.5%, e.g. less  
10 than 2%. Preferred polymers of the invention contain less than 2% by weight of water when they are saturated with water.

In a particularly preferred embodiment of this invention the thermoplastic polymers of the invention containing salt groups are crosslinked, particularly radiation-crosslinked, especially  
15 crosslinked in the presence of polyunsaturated monomers such as are disclosed in U.S. Patent Nos. 4,155,823, 4,353,961, 4,121,001 (now reissued as 31,103), and 4,176,027, the disclosures of which are incorporated by reference herein. Methods of incorporation of these monomers are well known and are disclosed in the above-referenced patents. Suitable radiation sources are high energy electron accelerators and gamma radiation sources. Preferred radiation doses are from 10 to 300  
20 KGy, particularly from 5 to 150 KGy.

As mentioned above, polymers of the invention are particularly useful as electrically insulating materials. In particular they may be used as insulative sheaths over electrical components, especially electrical conductors. These polymers are especially useful as insulation for wire and cable used for air  
25 frame wire and in electronic, computer and automotive applications. When used as wire insulation, the fluoropolymers may be used as a single layer or in a dual-wall configuration in which the second layer is the same or different from the first fluoropolymer layer. The fluoropolymers can be used in admixtures or compositions with various additives, such as antioxidants, stabilizers, pigments, and crosslinking agents.

30

The invention is illustrated by the following Examples, in which Examples 1 and 2 are comparative examples.

**EXAMPLE 1: Preparation of a 1:1 alternating ethylene-tetrafluoroethylene copolymer with pendant carbomethoxy groups (Comparative Example)**

5 In an evacuated and stirred one liter stainless steel autoclave are placed 750 ml of  $\text{CCl}_2\text{FCF}_2\text{Cl}$ , 3.0 ml of cyclohexane, and 5.0 g of  $\text{F}_2\text{C}=\text{CFO}(\text{CF}_2)_3\text{COOCH}_3$ . The temperature is adjusted to 60°C and the agitator speed is set at about 600 rpm. Tetrafluoroethylene (TFE) and ethylene gases are introduced into the reactor to give a composition of 70 mole% TFE and 30 mole% ethylene in the gas phase of the reactor at a total pressure of 6.3 kg/cm<sup>2</sup>. A 25 ml solution of 0.001 g/ml bis(perfluoropropionyl) peroxide initiator in  $\text{CCl}_2\text{FCF}_2\text{Cl}$  is prepared and injected into the reactor.

10 The concentrations of the gaseous TFE and ethylene are kept constant at a constant total pressure, and this monomer mixture is added to the autoclave continuously as the polymerization proceeds. At 10 min intervals an additional 7.5 ml of the peroxide solution is injected into the reaction mixture. The polymerization is allowed to proceed for a total of 80 min after the first addition of the initiator. The

15 pressure is vented, and the reactor content is removed and dried for 4 h under vacuum at 150°C yielding about 50 g of a colorless terpolymer.

**EXAMPLE 2: Preparation of a 1:1 alternating ethylene-tetrafluoroethylene copolymer with pendant Zn carboxylate groups (Comparative Example)**

20 A 1:1 alternating ethylene-tetrafluoroethylene polymer (PETFE) with pendant carbomethoxy groups was analyzed and found to contain 49.0 mole% repeat units derived from TFE, 49.0 mole% repeat units derived from ethylene, and about 2.0 mole% of carbomethoxy ester repeat units. Elemental analysis found: C, 35.55 and 35.31; H, 2.69 and 2.73; F, 60.84 and 60.72. The calculated values were: C, 36.27; H, 2.88; F, 59.04. The fluoropolymer was crystalline, melted at about 246°C (as determined by using a differential scanning calorimeter (DSC) in which the temperature increased at a rate of 10°C per minute) and displayed an infrared spectrum indicative of an ethylene-tetrafluoroethylene copolymer containing 2.1 mole% of carbomethoxy groups as indicated by the carbonyl band at 1786 cm<sup>-1</sup>. The carbomethoxy content was determined by comparative infrared analysis using a commercially available 1:1 alternating ethylene-tetrafluoroethylene copolymer containing controlled amounts of absorbed dimethyl perfluoroadipate. This polymer was pressed to a 10 mil (0.025 cm) thick film at 280°C. The film was placed in an autoclave together with a mixture of zinc acetate, acetic acid, water, and dodecafluoroheptanol (surfactant). The autoclave was heated for 18 h at 200°C. The thermoplastic fluoropolymer film was removed, washed, dried and then analyzed.

25 The polymer melted at 249°C. Its infrared spectrum showed a strong carboxylate carbonyl band at 1670 cm<sup>-1</sup>.

30

35

## EXAMPLE 3

The PETFE with pendant carbomethoxy groups of Example 2 was hydrolyzed to its Zn salt prior to melt processing using the following procedure. A monel autoclave (100 ml, Parr Instrument Co.) was charged with 2 g of zinc acetate dihydrate, 3.5 g of glacial acetic acid, 0.8 g dodecafluoro-1-heptanol surfactant, 50 ml of water, and 5.0 g of ester containing PETFE. The autoclave was purged with nitrogen and then heated for 16 h at 200°C followed by cooling to room temperature. The reactor content was filtered, then washed with water, ethanol, and then boiled in water containing 10% ethanol for two hours. The resin was dried at 150°C/1 mm Hg. Infrared analysis indicated essentially complete conversion of the ester to a carboxylate salt. The resin melted at 248°C, was extremely viscous and had high melt strength. A flexible and tough slab was molded at 280°C:

The mechanical properties at 150°C were determined on 10 mil (0.025 cm) slabs of three comparative examples, ETFE, radiation crosslinked ETFE (ETFE XL), ETFE with pendant carbomethoxy groups (Example 2), and one example of the invention, ETFE having pendant Zn carboxylate groups (Example 3). The results are shown in Table 1. For these tests, the Instron tensile tester was used at a test speed of one inch/min. The Table also shows estimates of the area under the curve of a plot of tensile stress against elongation, calculated by multiplying the Tensile Strength by the Elongation, and labelled "Area Under T/E Curve". This estimate, as is well known to those of ordinary skill in the art, is usually a good indication of the relative toughness of materials. All four polymers performed very well when tested according to ASTM D 3638-77, showing essentially identical resistance towards wet electrical tracking, i.e. they withstood the application of up to 330 drops of 0.1 molar aqueous ammonium chloride solution without failure.

25

TABLE I  
Mechanical Properties at 150°C

|                           | TENSILE STRENGTH |      | ELONGATION | AREA UNDER T/E CURVE |           |
|---------------------------|------------------|------|------------|----------------------|-----------|
|                           | PSI              | MPa  |            | (PSI x %)            | (MPa x %) |
| ETFE (Tefzel 2055)        | 1390             | 9.6  | 480        | 667200               | 4610      |
| ETFE XL (10 Mrad)         | 2260             | 15.6 | 120        | 271200               | 1872      |
| ETFE ester<br>(Example 2) | 1480             | 10.2 | 640        | 947200               | 6528      |
| ETFE Zn salt (Example 3)  | 4050             | 28.0 | 390        | 1579500              | 10920     |

**EXAMPLE 4**

This example illustrates radiation grafting of ETFE with ethyl acrylate. Twenty grams of a commercial ETFE resin powder (Tefzel 2010, Du Pont) in 50 ml of ethyl acrylate were heated under reflux for 4 h under nitrogen in the presence of 2.5% phenolic inhibitor (Irganox 1010). The swollen resin product was filtered, subjected to repeated vacuum degassing to reduce the monomer content to about 10%, and then purged with nitrogen to remove all oxygen. The dried resin was then sealed under nitrogen into a double polyethylene bag, irradiated with electrons from a 1 MeV source at a dose rate of 3.75 Mrads/min to a total dose of 12 Mrads, and then annealed at 110°C for 1 hour under nitrogen. The resin product was thoroughly leached with tetrahydrofuran and then dissolved in diisobutyl adipate (150 ml) at about 240°C. All of the resin was found to dissolve. The solution was slowly cooled. It gave a hazy gelatinous precipitate which was filtered, washed with diisobutyl adipate, leached with tetrahydrofuran, and then dried at 150°C at 1 mm Hg. The dried resin was compression molded at 280°C to give a tough slab. An infrared analysis indicated 1.5 to 2 mole% of ester incorporation (ester carbonyl band at 1736 cm<sup>-1</sup>).

**EXAMPLE 5**

The same conditions as Example 4 were run with diethyl fumarate as the graft monomer.

20 Similar results were obtained.

**EXAMPLE 6**

The ester-grafted ETFE resins of Examples 4 and 5 were converted to their corresponding zinc salts. A monel autoclave (100 ml, Parr Instrument Company) was charged with 1.2 g of zinc acetate dihydrate, 1.5 ml of glacial acetic acid, 50 ml of water, 0.4 g of dodecafluoro-1-heptanol surfactant and 1.0 to 2.0 g of graft polymer. The autoclave was purged with nitrogen and then heated at 195 to 200°C for 20 h. After cooling, the reactor content was filtered and the filter residue was extensively washed with water and methanol and then dried. The resulting resin powder was compression molded at 280°C to give a tough and flexible slab. Infrared analysis indicated greater than 90% conversion of the ester to the corresponding salt (ester carbonyl band at 1740 cm<sup>-1</sup>, carboxylate carbonyl band at 1590 cm<sup>-1</sup>). The Zn carboxylate containing ETFE resins showed substantially increased melt viscosities and melt strength compared to the ETFE starting materials.

## EXAMPLE 7

This example illustrates the improved wire cut through resistance of a 1:1 alternating ethylene-tetrafluoroethylene polymer with pendant zinc carboxylate groups. A 20 AWG stranded copper conductor wire is extrusion-coated with the ETFE containing pendant carbomethoxy groups of Example 2. The wall thickness of the insulation is 10 mils. This wire insulation is converted to its zinc salt according to the procedure described in Example 2. A standard wire cut through test is conducted at 150°C using a 90° blade with a 0.005" radius at the apex. The cut-through resistance for this ETFE ionomer (about 0.5 lb/mil; 89.5 kg/cm) is higher than that of standard ETFE (0.4 lb/mil; 71.6 kg/cm).

## EXAMPLE 8

This example illustrates the preparation and properties of a ETFE ionomer with pendant zinc sulfonate groups. A polymer prepared by copolymerizing ethylene, tetrafluoroethylene, and a perfluoromonomer having a terminal sulfonyl fluoride group, melted at 250°C and was found to contain 1.9 percent of sulfonyl groups. (For purposes of this mole% calculation, every double bond incorporated in the polymer backbone, e.g. -CF<sub>2</sub>-CF<sub>2</sub>-, -CH<sub>2</sub>-CH<sub>2</sub>-, and -CF<sub>2</sub>-CF-, is counted.) The resin had a melt index of 11.5 g/10 minutes (as determined following the procedure of ASTM D-3307), a tensile strength of 6060 psi (41.8 MPa), and an elongation of 390%, both measurements being made at room temperature. The resin was compression molded at 280°C to give a 10 mil (0.025 cm) thick slab. This slab was placed in an autoclave and treated with a zinc acetate solution as described in Example 2 but with the addition of pyridine (in a catalytic amount) and at a temperature of 215°C for 48 hours to yield a polymer with pendant zinc sulfonate groups. The zinc treated polymer, unlike the starting polymer, did not exhibit a medium strong infra-red band attributable to the sulfonyl fluoride group at 820 cm<sup>-1</sup>. The mechanical properties of this ETFE zinc sulfonate ionomer and the starting ETFE with pendant sulfonyl groups are shown in Table II.

## EXAMPLE 9

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The procedure of Example 2 was applied to a film of a ETFE which contained 4.0 mole% of pendant perfluorocarbomethoxy groups to obtain the corresponding ETFE zinc carboxylate ionomer. The mechanical properties of this ETFE ionomer are shown in Table II.

**EXAMPLE 10**

The ETFE with pendant sulfonyl fluoride groups was hydrolysed to the magnesium salt by the procedure of Example 2 except that magnesium acetate was used instead of zinc acetate and the 5 autoclave was heated at 215°C for 48 hours. The mechanical properties of this ETFE ionomer are shown in Table II.

TABLE II  
Mechanical Properties at 150°C

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| Example                    | TENSILE STRENGTH |      | ELONGATION % | AREA UNDER T/E CURVE |           |
|----------------------------|------------------|------|--------------|----------------------|-----------|
|                            | PSI              | MPa  |              | (PSI x %)            | (MPa x %) |
| 8: pendant sulfonyl groups | 2310             | 15.9 | 800          | 1848000              | 12720     |
| 8: Zn sulfonate ionomer    | 4115             | 28.4 | 440          | 1810600              | 12496     |
| 9: Zn carboxylate ionomer  | 4860             | 33.5 | 350          | 1701000              | 11725     |
| 10: Mg sulfonate ionomer   | 3550             | 23.1 | 340          | 1207000              | 7854      |

**EXAMPLE 11**

A polymer prepared by copolymerizing ethylene, tetrafluoroethylene and a 15 perfluoromonomer having a terminal sulfonyl fluoride group was found to contain 2.4 mole% sulfonyl groups. The polymer was extruded onto 20 AWG silver-coated copper wire to give an insulated wire with an 0.008 inch (0.020 cm) wall thickness of polymer. Fifteen feet (4.57 meters) of the coated wire were refluxed at 96°C for 24 hours in a N<sub>2</sub> atmosphere in a 2000 ml resin kettle containing 250 ml pyridine, 250 ml water, and 25 g barium acetate. (The ends of the wire were kept outside the kettle in order to prevent corrosion.) The conductor was then rinsed with water, refluxed in a solution of water and 10% acetic acid for 4 hours to extract contaminants, and dried in a vacuum oven for 4 hours at 150 to 20 160°C. The physical properties of the final material are shown in Table III.

**EXAMPLES 12 to 25**

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Following the procedure of Example 11, a number of other compositions were prepared. The starting material varied in mole% sulfonyl groups from 0 to 3.9%. A variety of metal acetates were used to prepare ionomers containing different cations. The physical properties of the prepared compositions, a commercially available ETFE polymer (Tefzel™ 280 and Tefzel™ 2055, available from 30 E. I. duPont de Nemours), and the starting polymers are presented in Table III. In some cases, the

measurements were made on compression-molded slabs of material. These data are presented for comparison and are indicated by a † symbol.

TABLE III  
Physical Properties of PETFE-SO<sub>3</sub>M Ionomers

| Example          | %SO <sub>3</sub> F | Cation           | CTR<br>150°C<br>lb/mil | Tensile<br>psi<br>150°C | Elonga-<br>tion %<br>150°C | Tensile<br>psi<br>25°C | Elonga-<br>tion %<br>25°C | H <sub>2</sub> O<br>Uptake<br>% |
|------------------|--------------------|------------------|------------------------|-------------------------|----------------------------|------------------------|---------------------------|---------------------------------|
| Tefzel<br>280    | 0                  | 0                | 0.40                   | 2320                    | 420                        | 7880                   | 253                       | <0.1                            |
| Tefzel<br>280 †  | 0                  | 0                |                        | 1764                    | 553                        |                        |                           |                                 |
| Tefzel<br>2055 † | 0                  | 0                |                        | 1580                    | 543                        | 6726                   | 324                       |                                 |
| †                | 1.2                | 0                |                        | 2362                    | 640                        |                        |                           |                                 |
|                  | 2.1                | 0                | 0.27                   | 1750                    | 510                        | 6690                   | 267                       |                                 |
| †                | 2.1                | 0                |                        | 1886                    | 730                        |                        |                           |                                 |
|                  | 2.8                | 0                | 0.33                   | 2900                    | 647                        | 7430                   | 245                       |                                 |
| †                | 3.9                | 0                |                        | 2899                    | 750                        |                        |                           |                                 |
| 11               | 2.4                | Ba <sup>2+</sup> | 1.03                   | 4350                    | 240                        | 9050                   | 204                       |                                 |
| 12               | 2.1                | Ba <sup>2+</sup> | 0.88                   | 4011                    | 223                        | 7980                   | 157                       | 3.2                             |
| 13               | 2.8                | Ba <sup>2+</sup> | 1.28                   | 4400                    | 213                        | 9420                   | 150                       | 4.5                             |
| 14               | 2.1                | Na <sup>1+</sup> | 0.58                   | 3660                    | 280                        |                        |                           | 4.1                             |
| 15               | 2.1                | Ca <sup>2+</sup> | 0.87                   | 4490                    | 253                        | 8670                   | 150                       | 3.5                             |
| 16*              | 2.1                | Ca <sup>2+</sup> | 0.75                   | 4370                    | 157                        |                        |                           |                                 |
| 17               | 2.1                | Sr <sup>2+</sup> |                        | 4330                    | 203                        | 9200                   | 148                       | 3.7                             |
| 18               | 2.1                | Mn <sup>2+</sup> |                        | 4450                    | 260                        | 8580                   | 148                       | 4.7                             |
| 19               | 2.1                | Co <sup>2+</sup> |                        | 4350                    | 237                        | 9190                   | 133                       | 4.1                             |
| 20               | 2.1                | Ni <sup>2+</sup> |                        | 4090                    | 267                        | 9670                   | 165                       | 3.4                             |
| 21               | 2.8                | Ni <sup>2+</sup> | 0.67                   | 3840                    | 314                        | 9651                   | 175                       | 3.0                             |
| 22               | 2.1                | Zn <sup>2+</sup> | 0.46                   | 3340                    | 337                        |                        |                           | 2.5                             |
| 23               | 2.1                | Pb <sup>2+</sup> | 0.68                   | 4320                    | 310                        |                        |                           |                                 |
| 24               | 2.1                | La <sup>3+</sup> | 0.59                   | 3320                    | 377                        |                        |                           |                                 |
| 25               | 2.4                | Yb <sup>3+</sup> | 0.43                   | 3244                    | 403                        | 8781                   | 240                       | 1.8                             |

5    † Compositions tested in slab form.

\* Prepared with calcium benzoate.

What is claimed is:

1. A thermoplastic fluoropolymer which

- (A) has a yield strength at 150°C of at least 400 psi (2.76 MPa);
- (B) has a tensile strength at 150°C of at least 3500 psi (24.1 MPa); and
- (C) fulfills at least one of the following conditions
  - (1) it is electrically insulating;
  - (2) when saturated with water it contains less than 5 percent by weight of water; and
  - (3) it does not track when tested in accordance with ASTM D3638.

2. A fluoropolymer according to claim 1 which has a yield strength of at least 500 psi (3.45 MPa) and a tensile strength of at least 3700 psi (25.5 MPa).

3. A thermoplastic fluoropolymer which

- (A) is an ionomer which comprises
  - (1) at least 40 mole percent perfluorinated repeat units; and
  - (2) at least 0.4 mole percent repeat units which contain at least one anion of a salt group;
- (B) has a yield strength at 150°C of at least 400 psi (2.76 MPa); and
- (C) has a tensile strength at 150°C of at least 2000 psi (13.8 MPa); and
- (D) fulfills at least one of the following conditions
  - (1) it is electrically insulating;

- (2) when saturated with water it contains less than 5 percent by weight of water; and
  - (3) it does not track when tested in accordance with ASTM D3638.
4. A fluoropolymer according to claim 1 or 3 which is covalently crosslinked.
5. A fluoropolymer according to claim 1 or 3 which further has a cut-through resistance at 150°C of at least 0.6 lb/mil (107 kg/cm).
6. A fluoropolymer according to claim 1 or claim 3 in which the fluoropolymer is an ethylene-tetrafluoroethylene copolymer.
7. A fluoropolymer according to claim 3 wherein each of the salt groups is a salt of a carboxylic, sulfonic, or phosphonic acid, wherein if the salt group is a salt of a sulfonic acid, the polymer is substantially fully neutralized.
8. A fluoropolymer according to claim 8 wherein each of the salt groups has the formula  $-(XP^r)^q(M^{r+})_s$ , wherein
- (a) X is the anion of an acid group,
  - (b) M is a cation,
  - (c) each of p and s is 1 or 2 and each of q and r is 1 to 6, and
  - (d) pq = rs.
9. A fluoropolymer according to claim 8 wherein the polymer comprises at most 6 mole percent repeat units which contain at least one anion of a salt group.
10. An insulated wire which comprises
- (A) a center conductor which is electrically conductive; and
  - (B) a composition which surrounds at least part of the center conductor and which comprises a fluoropolymer according to claim 1 or 3.

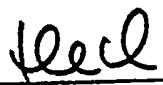
11. A method of making a thermoplastic fluoropolymer according to claim 1 or 3, which method comprises

- (1) copolymerizing a mixture of monomers comprising
  - (a) a first ethylenically unsaturated perfluorinated monomer, and
  - (b) a second unsaturated monomer which comprises at least one functional group which (i) is an acid group, or (ii) can be converted into an anion of an acid salt group; and
- (2) converting at least some of the functional groups into salt groups so that the resulting copolymer contains x mole percent of repeat units containing anions of salt groups and y mole percent of repeat units containing acid groups,

wherein x is at least 0.4 and y is at most 8.0 and (x + y) is at most 8.4.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 90/03485

|   |   |                                     |
|---|---|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>   |   |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC<br>IPC5: C 08 F 214/26, H 01 B 3/44   |   |                                     |
| <b>II. FIELDS SEARCHED</b>  |   |                                     |
| Minimum Documentation Searched <sup>7</sup>   |   |                                     |
| Classification System   | Classification Symbols  |                                     |
| IPC5  | C 08 F; H 01 B  |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in Fields Searched <sup>8</sup>   |   |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>   |   |                                     |
| Category <sup>10</sup>  | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>  | Relevant to Claim No. <sup>13</sup> |
| A   | EP, A1, 0002809 (HOECHST AKTIENGESELLSCHAFT)<br>11 July 1979, see abstract<br>see page 13, lines 9-22, page 19, table<br>I, page 20 lines 12-20<br><br>--   | 1-2,<br>10                          |
| A   | EP, A2, 0151885 (E.I. DU PONT DE NEMOURS AND<br>COMPANY) 21 August 1985,<br>see page 5, line 28 - line 31;<br>page 7, line 24 - line 31; abstract<br><br>-- | 1, 10,<br>11                        |
| A   | EP, A1, 0124378 (E.I. DU PONT DE NEMOURS AND<br>COMPANY) 7 November 1984,<br>see page 6, line 10 - line 18;<br>abstract<br><br>--                           | 1                                   |
| <b>* Special categories of cited documents:</b> <sup>10</sup><br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed<br><br><b>"T"</b> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br><b>"X"</b> document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<br><b>"Y"</b> document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br><b>"&amp;"</b> document member of the same patent family |   |                                     |
| <b>IV. CERTIFICATION</b>  |   |                                     |
| Date of the Actual Completion of the International Search   | Date of Mailing of this International Search Report   |                                     |
| 5th October 1990  | 24. 10. 90  |                                     |
| International Searching Authority<br>EUROPEAN PATENT OFFICE   | Signature of Authorized Officer<br>F.W. HECK                           |                                     |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |   |                      |
|--|---|----------------------|
| Category   | Citation of Document, with indication, where appropriate, of the relevant passages  | Relevant to Claim No |
| A  | US, A, 4624990 (LUNK ET AL) 25 November 1986,<br>see abstract<br><br>--   | 1,8                  |
| A  | Patent Abstracts of Japan, Vol 9, No 59, C270,<br>abstract of JP 59-196308, publ 1984-11-07<br>(DAIKIN KOGYO K.K.)<br><br>----- | 3,6,7,8              |

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 90/03485

SA 38264

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on 28/08/90  
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| Patent document cited in search report | Publication date | Patent (family member(s))                              |  | Publication date   |
|--|------------------|--|--|--|
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| EP-A2- 0151885                         | 21/08/85         | JP-A-<br>US-A-   | 60156632<br>4675453  | 16/08/85<br>23/06/87   |
| EP-A1- 0124378                         | 07/11/84         | CA-A-<br>DE-A-<br>JP-C-<br>JP-A-<br>JP-B-<br>US-A-     | 1234151<br>3473282<br>1456608<br>59207911<br>63002964<br>4522995 | 15/03/88<br>15/09/88<br>09/09/88<br>26/11/84<br>21/01/88<br>11/06/85 |
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For more details about this annex : see Official Journal of the European patent Office, No. 12/82